

Electrical Conduction in Nonlinear Composites

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Introduction

Composite systems constitute a large class of naturally occurring or artificially synthesized disordered systems [1]. The systems are microscopically inhomogeneous and disordered but look homogeneous on the macroscopic scale. From the tunnelling electron micrographs (TEM) of such a composite material it can be seen that the typical dimension (ξ) of metallic islands embedded in the insulating matrix are much greater than the atomic size (a) but obviously much smaller than the macroscopic scale length (L): $a \ll \xi \ll L$. The effective conductivity of such a system depends upon the conductivities of the individual phases. For a low volume fraction (p) of the conducting phase, the system as a whole behaves like an insulator since the conducting regions do not form a continuous path through the sample. As p is increased, the conducting regions will in general tend to grow and eventually at a critical volume fraction (p_c , called the percolation threshold) the conducting phase *percolates* through the sample. This may be considered as a classical insulator-to-metal transition or more popularly as a *percolation transition*. For all $p > p_c$, the system is metallic, and if the conducting phase is Ohmic, so is the whole macroscopic system. Clearly this class of systems may be well described by the geometrical percolation theory.

Now if an external voltage is applied across such composite systems (examples include dispersed metallic systems, carbon-black-polymer composites, sulphonated (doped) polyaniline networks *etc.*, which are usually highly structured and give rise to some sort of universal behaviour.) a wide variety of **interesting features** associated with a nonlinear response emerge. Usually these composites exhibit an unusually *low percolation threshold*. Qualitatively *identical nonlinear $I - V$ (as well as $dI/dV \equiv G$) against V* response have been reported [2, 3] both below and above the threshold for many of the composites although the nonlinearity exponent is found to be grossly different in the two regimes. Power-law growth of excess conductance for small V is another general feature of the class of composite systems where non-integer power-law has been observed. This in turn implies a power-law in the $I - V$ relationship for small applied voltage (V). The $G - V$ curves are seen to *saturate* for an appropriately high enough voltage below the Joule-heating regime. The typical curve then looks like a nonlinear sigmoidal type function interpolating two linear regimes. Recent experiments on carbon-wax systems [2] as well as many earlier ones on disordered/ amorphous systems [4], find a non-integer power-law behaviour and a saturation in the DC-response as mentioned above. Composite systems show very interesting temperature-dependent conduction properties particularly in the low

temperature regime where the conduction is mainly due to phonon-assisted hopping (Mott's variable range hopping (VRH)). Some recent experiments indicate an effect of dilution on the relevant temperature-exponent for fitting the low-temperature data with VRH or its other variations. We address many of the above mentioned features through our study.

Modelling Nonlinear Transport

The framework of our study is based on percolation theory. The ultra-low percolation threshold and the fact that many of these nonlinear systems carry current even below p_c indicates strongly that *tunnelling* through disconnected (dispersed) metallic regions must give some virtually connected percolating clusters. From the nonlinear $I - V$ characteristics (*e.g.*, see the experiment by Chen and Johnson [3]) it is observed that the response (DC) behaviour is reversible with respect to the applied field. Also the temperature-dependent resistance with a minimum at some characteristic temperature and the Mott variable range hopping (VRH) type behaviour at very low temperatures give further credence to tunnelling assisted percolation. In practice, the tunnelling conductance should fall off exponentially with distance and hence the tunnelling should have an upper cut-off length scale. So for simplicity and to capture the basic physics, we construct a bond (lattice) percolation model for this problem, such that tunnelling may take place only between two nearest neighbour ohmic bonds and no further. For a further simplification, we assume the nonlinear response of each tunnelling bond (or resistor) to be piecewise linear. We assume that all the tunnelling bonds have an identical voltage threshold (v_g) below which they are perfect insulators and above which they behave as ohmic conductors. Clearly this is the source of nonlinearity in the model. Made of both random resistive and tunnelling elements, this network will be called a random resistor cum tunnelling-bond network (RRTN) ¹.

The **percolation statistics** [5] of the model network is examined in the saturation limit, *i.e.*, when all the tunnelling bonds can overcome their threshold. We estimate the new percolation (p_{ct}) threshold and address the question of universality class. We undertake small-cell renormalization, Monte Carlo simulation and finite size scaling analysis to estimate p_{ct} and some of the independent critical exponents around it. The simulation results are obtained for lattices in 2D for convenience. Lattice sizes $L = 20$ to 300 are considered. The p_{ct} is found to be 0.181 ± 0.001 and the value of correlation length exponent ν is obtained to be $\cong 1.35 \pm 0.06$. The *fractal dimension* (D) for the spanning cluster at the threshold which is found to be $D \cong 1.87$, very close to $91/48$, the fractal dimension for 2D random bond percolation. We also calculate the *conductivity exponent*, t , in the upper linear regime where all the tunnelling resistors

¹In this respect we comment that a dynamic random resistor (DRRN) model proposed by Gefen *et al.*, [1] is different from our RRTN model in the sense that they allowed any insulating bond at any position in the lattice to break and turn metallic, whereas in our case such breakings can occur only at some correlated bond positions. Moreover, with the addition of these bridge bonds (anywhere), the new percolation threshold may not be properly defined like that of ours.

are considered to be behaving as the other ohmic resistors. We obtain $t/\nu \cong 0.90$, where the value of this ratio for the usual percolation problem is $\cong 0.97$. The value of the critical exponents, as obtained above, indicate that this correlated model for percolation belongs to the same *universality class* as that of its uncorrelated version (in the absence of tunnelling bonds).

An **effective medium approximation (EMA)** [6] has been used to calculate the percolation threshold for our model system and the conductivity behaviour in the saturation limit. The probability of a bond to be ohmic, tunnelling or purely insulating according to the considerations of our model is: $P_{ohm} = p$, $P_{tun} = (p^3 + 3p^2q + 3pq^2)^2q$, $P_{ins} = [1 - (p^3 + 3p^2q + 3pq^2)^2]q$, where $q = 1 - p$. If the conductances of the three types of bonds are denoted by g_{ohm} , g_{tun} and g_{ins} , the EMA equation for this general situation can be written as

$$\frac{P_{ohm}(G_e - g_{ohm})}{[g_{ohm} + (d-1)G_e]} + \frac{P_{tun}(G_e - g_{tun})}{[g_{tun} + (d-1)G_e]} + \frac{P_{ins}(G_e - g_{ins})}{[g_{ins} + (d-1)G_e]} = 0. \quad (1)$$

Solving the above equation for 2D ($d = 2$) and 3D ($d = 3$) we obtain $p_{ct} = 1/4$ and $1/8$ respectively. It may be noted that the value of p_{ct} in 2D is close to that obtained by numerical simulation. We examine the behaviour of the effective linear conductance (G_e) for the macroscopic model composite system in the saturation limit, given some specific values or forms of the resistive elements. These then are compared with the results obtained with the numerical simulation. The agreement is fairly good when one is away from the threshold, p_{ct} .

Next we study the **dielectric breakdown** phenomenon in our model as the onset of nonlinear conduction against applied field for $p \leq p_c$. Below the percolation threshold (p_c) there exists a number of metallic clusters, isolated from each other, but closely spaced. As new conducting paths are created when the local electric field across tunnelling bonds increases above v_g , the conductivity of the whole system jumps from a zero to a non-zero value (for $p < p_c$) as the external applied field crosses [7] the dielectric breakdown field ($E_B^p = V_B^p/L$). Note however that below p_{ct} there is no sample-spanning cluster of combined ohmic and tunnelling bonds, and hence there is no breakdown at any finite electric field according to the criterion set for our model. The interest would be to estimate the breakdown exponent t_B , where $E_B^p \sim (p_c - p)^{t_B}$. To remove finite size effects, we work with the asymptotic breakdown field $E_B^p(L = \infty)$. From the least-square fit of the data for the above we find that the breakdown exponent $t_B \cong 1.42$ for our RRTN model. It seems that the above exponent t_B is not very different from that of the usual breakdown exponent $t_B = \nu = 1.33$ as discussed above. But it is not unlikely either that we have a different result in our hands. If different, it could be because of the nature of the electric field in increasing the effective volume fraction of the conductors.

We present the **nonlinear DC-response** [7] namely, the current-voltage ($I - V$) and the conductance-voltage $G - V$ characteristics in our model system. Our computer simulation involves solving Kirchhoff's law of current at the nodes of the RRTN network in 2D with the linear and nonlinear (assumed piecewise linear) resistors and

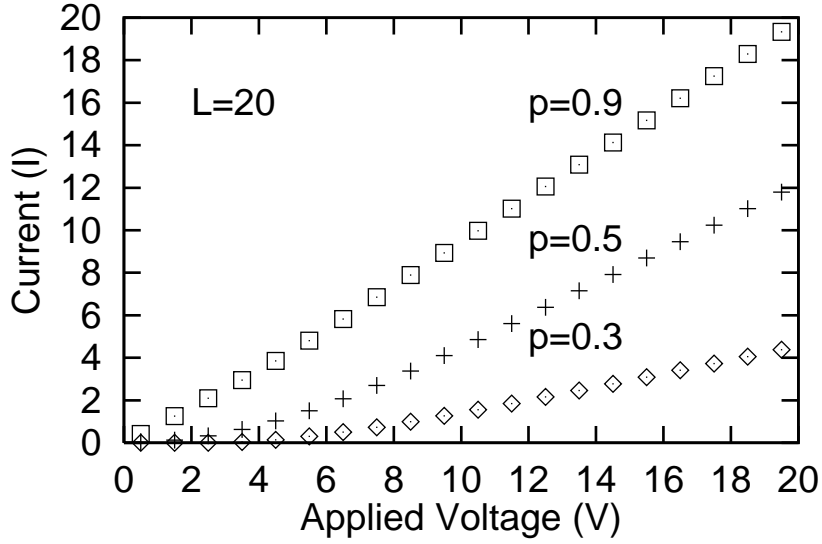


Figure 1: Current (I) against Voltage (V) curves for different volume fractions (p) of the conducting components.

the standard Gauss-Seidel relaxation technique. We obtain current (I) and therefrom the differential conductance ($G = dI/dV$) for the whole network at a given volume fraction p of the ohmic bonds. Simulation results for nonlinear $I - V$ curves for a square network of size $L = 20$ were plotted in **fig. 1** for $p = 0.3, 0.5$ and 0.9 . Averages over 50 configurations are done in each case. One may note that the nonlinearity in the response exists for all p both below and above p_c .

The differential conductance G ($\equiv dI/dV$) of the network is obtained directly from the $I - V$ curves. A typical such $G - V$ curve is shown in **fig. 2** for $L = 20$ and $p = 0.8$. To understand the conductance behaviour for the entire network we adopt a pedagogical approach where we analyse the elementary prototype circuits with nonlinear resistors. The conductance (G) of these elementary units grows nonlinearly with the applied voltage V and gives us an idea of what type of functions may be used to fit the $G - V$ data for the much more complex macroscopic system. After sifting through various such functional forms, we find that the simulation data obtained through our model system in 2D were best fitted with:

$$G = G_0 + G_d[1 - \exp(-\lambda\Delta V^\mu)]^\gamma, \quad (2)$$

where $G_d = G_f - G_0$ and $\Delta V = V - V_g$, where V_g is the macroscopic threshold voltage and is the same as V_B above. G_0 is the conductance in the limit $\Delta V \rightarrow 0$. Experimentally G_f may be obtained by applying a large enough voltage (V_s) such that Joule heating remains unimportant. In our computer simulation on finite sized systems, we find V_s to be many orders of magnitude larger than V_0 and G_f is the conductance when all the tunnelling bonds take part in the conduction.

For a meaningful comparison of all the $G - V$ data with different G_0, G_f, V_g , etc., we scale the conductance G as $\tilde{G} = (G - G_0)/G_d$ and the voltage V as $\tilde{V} = (V - V_g)/V_g$.

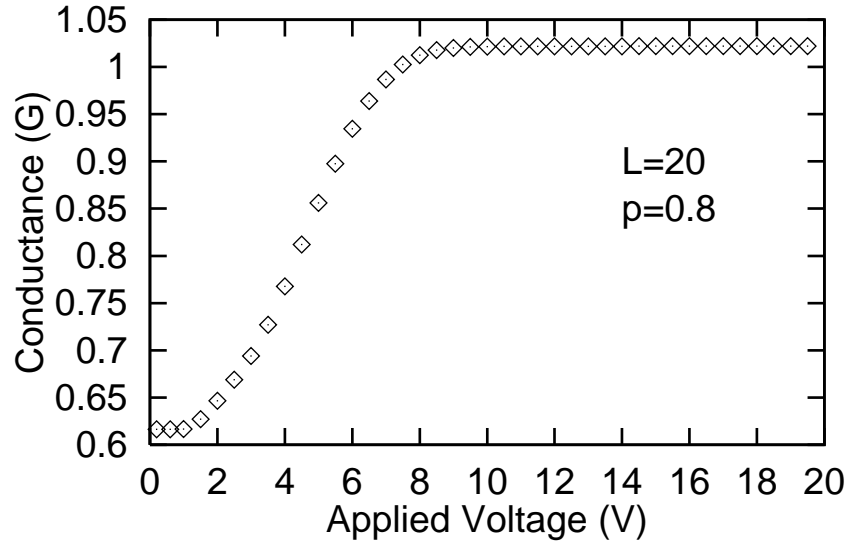


Figure 2: A typical curve showing the behaviour of differential conductance G against V .

In fact, we tried to scale the $G - V$ data for a set of p in the range $0.48 \leq p \leq 0.52$ (*i.e.*, both below and above p_c), and we found that all the data do reasonably collapse. This suggests the following general form for the functional behaviour close to p_c ;

$$\tilde{G} = f(\tilde{V}), \quad (3)$$

where $f(x)$ is a function such that $f(0) = 0$, and $f(\infty) = 1$. Here we point out that the threshold (or the breakdown) voltage V_g is the only relevant voltage scale that enters into the scaling function. The other voltage scale V_s is seen to have no role in the above scaling eqn. (3). Expanding eqn. (2) near the onset of nonlinearity ($\Delta V \rightarrow 0$), the excess conductance $\Delta G = G - G_0$ varies with the voltage difference (ΔV) as a power-law:

$$\Delta G \sim \Delta V^{\mu\gamma} = \Delta V^{\delta}, \quad (4)$$

and the nonlinearity exponent $\delta = \mu\gamma$. For p close to p_c ($0.48 \leq p \leq 0.52$) we find that $\delta \cong 1.0$. Thus the nonlinearity exponent for the $I - V$ curve is $\alpha = \delta + 1 \cong 2.0$. Experiments in 2D arrays of normal metal islands connected by small tunnel junctions by Rimberg *et al.* [1] found $\alpha = 1.80 \pm 0.16$; suggesting a good support for our model.

Our analysis of results for widely different volume fractions indicate that the nonlinearity exponent δ increases significantly as we go sufficiently away (both below and above) from the percolation threshold. The scaled data for all the curves now do not fall on top of each other indicating that all of them can not be described by the same fitting function $f(x)$ or by the same fitting parameters μ and γ . Hence the possible power-law in the regime ($\Delta V \rightarrow 0$) for the onset of nonlinearity for these curves of different p are *not* all the same.

Now the difference between two limiting conductances, $G_d = G_f - G_0$ may be taken as a measure of *overall nonlinearity*, whereas the nonlinearity exponent (δ or

α) gives a measure of the *initial nonlinearity* near the threshold. G_d as a function of p shows a peak at around $p = p_c$. So we find that the overall nonlinearity is maximum near the geometrical percolation threshold. Next we looked at how G_d is related to the initial conductance G_0 in the interval $p_{ct} < p < 1$ in the limit $L \rightarrow \infty$. The relationship is linear which actually means that G_f is also linearly dependent on G_0 . This in turn implies an identical p -dependence for the two saturation conductances G_0 and G_f around their respective thresholds (p_c and p_{ct}), consistent with the fact that the system has the same conductivity exponent in both the zero and the infinite voltage limits (*i.e.*, $G_{0,f} \sim (p - p_{c,ct})^t$).

The **AC-response** of the model system also turns out to be very interesting. In this case the tunnelling bonds in RRTN are assumed to behave as capacitors. The AC-conductance is now expected to behave nonlinearly between two saturation regions of $\omega \rightarrow 0^+$ and $\omega \rightarrow \infty$ as in the case of DC-response discussed above. We first give here the EMA where each tunnelling bond has the conductance $g_{tun} = i\omega c$, where $i = \sqrt{-1}$, c is the capacitance of the tunnelling bonds and ω is the circular frequency of the applied sinusoidal voltage with unit amplitude. Here we take $c = 1$ for convenience, thereby setting the frequency scale. So for a square lattice ($d = 2$) if we take $g_{ohm} = 1$ in eqn. (1), the real part of $G_e(\omega)$ can be shown to be

$$ReG_e(\omega) = \frac{(2P_{ohm} - 1)}{2} + \frac{1}{2}(X^2 + Y^2)^{1/4} \cos \frac{\theta}{2}, \quad (5)$$

where $X = (2P_{ohm} - 1)^2 - \omega^2(2P_{tun} - 1)^2$ and $Y = 2\omega[(2P_{ohm} - 1)(2P_{tun} - 1) - 2(2P_{ins} - 1)]$ and $\theta = \tan^{-1}(Y/X)$. It may be checked from the above eqn. (5) that at $p = p_c$ ($= 1/2$ in 2D) and in the limit $\omega \rightarrow 0$ the real part of the complex effective conductance behaves as $ReG_e(\omega) \sim \omega^{0.5}$. This is also true for 3D.

Next we look at the simulation results for the AC-response. It has been observed that for frequencies $\omega < \omega_0$, one gets some generic linear or quadratic dependences on ω which may be easily understood. But, for frequencies $\omega > \omega_0$, we expect percolative effects to gain control and $G_{rms}(\omega)$ to follow an equation similar in form to that used for the DC-conductance:

$$G_{rms}(\omega) = G_{rms}(\omega_0) + G_d(\omega)[1 - \exp(-\lambda[\omega - \omega_0]^\mu)]^\gamma. \quad (6)$$

For many practical situations, the intermediate frequency range (between ω_0 and the upper saturation) is of prime interest. In this case, fitting the average graphs, we find that $\delta' (= \mu\gamma)$ has a minimum value of about 0.7 near p_c , and increases on both sides of it. In other words, the AC nonlinearity exponent δ' (away from p_c) is also p -dependent. Notwithstanding this fact, experiments [2, 4] on a wide variety of disordered systems observe $\delta' \cong 0.7$ which matches closely with our result.

The behaviour of phase-angle (sometimes called the loss-angle) of the complex conductance $G_e(\omega)$ with respect to frequency (ω) is of practical interest. The phase-angle (ϕ) is defined through $\tan \phi = ImG_e(\omega)/ReG_e(\omega)$. The shift of the peak value of it with the dilution (p) is worth noting. The agreement between the simulation result and that by EMA is reasonably good. The variation of the phase-angle (ϕ)

with frequency (ω) has been observed for a range of values $0.3 < p < 0.7$. The peak value $\phi_m \cong 0.7$ (radian) is obtained for p around p_c which is close to the universal phase-angle value of $\pi/4$ obtained in the simple RC model in 2D at p_c predicted by Clerc *et. al.* [8]. We looked at the phase-angle versus frequency for $p \cong p_c$, and we find therefrom that $\phi_m \cong 0.7$ in this model too.

Composite systems have very interesting **temperature dependent conduction** properties [9] particularly in the low-temperature regime. Some recent experiments on them show the analysis of their low-temperature data which seem to be confusing and contradicting each other. The controversy, as briefly described below, is still on and the complete physics is yet to be understood. The usual attempt is to fit the low-temperature data for such systems by the well-known Mott variable range hopping (VRH) formula or with any of its many generalized forms. In a very recent experiment by Reghu *et al.*, [9] in proton-doped polyaniline networks, it was found that the exponent in VRH systematically increases from 0.25 to 1 upon decreasing the volume fraction p of the conducting component. Here our goal is not to explain the recent experimental results exactly. Rather, our modest hope is to demonstrate the fact that if one represents the low-temperature data in such systems by the VRH or any of its generalized forms, then the the relevant exponent in that can change continuously with dilution. The approach is again based on percolation theory where we assume the the activated behaviour for the tunnelling bonds and the metallic behaviour to the ohmic bonds. The effect of dilution of the temperature dependent conductance behaviour can thus be understood at a preliminary level [10].

Discussion

In this report we have discussed various aspects of the nonlinear response in the disordered binary composite systems in general. We have proposed a very simple and minimal model in order to understand the nonlinear electrical response and associated physics in composite systems. In many other physical systems, the response is negligibly low (or there is no response at all) until and unless the driving force exceeds a certain threshold value. So a class of problems exist where sharp thresholds to transport occur. The examples in the electrical case is a Zener diode and in the fluid permeability problems a Bingham fluid (where there is a critical shear stress τ_c , above which it has a finite viscosity and below which it is so enormously viscous that it does not flow). So all these problems may be treated in a similar footing with the underlying percolation geometry.

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